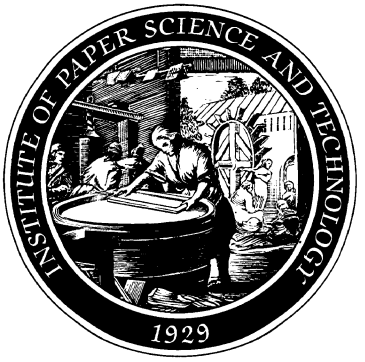

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Pulp Properties Influencing Oxygen Delignification Bleachability

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PULP PROPERTIES INFLUENCING OXYGEN DELIGNIFICATION BLEACHABILITY

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ABSTRACT

The influence of peracetic acid pretreatment and interstage treatment on subsequent oxygen delignification was evaluated for both kappa 24 and 47 softwood kraft pulps. Both pulps were oxygen delignified under standard (~ 42% delig.) and aggressive (~ 68% delig.) conditions. Selected pulps were also pretreated with distilled peracetic acid under slightly alkaline conditions (pH = 8). Peracetic acid pretreatment was found to increase the efficiency of the oxygen delignification stage with no loss of pulp viscosity. A kappa 47 pulp could be oxygen delignified under aggressive conditions to give a pulp of comparable viscosity and brightness as standard oxygen delignified kappa 24 pulp. The fundamental chemistry of the process was studied by ^{1}H–, ^{13}C–, ^{19}F–, and ^{31}P–NMR spectroscopy. Residual lignin quinone contents were quantified by trimethylphosphite/^{31}P–NMR and ^{19}F–NMR spectroscopy. Oxygen delignification conditions were found to have little influence on the introduction of colored quinone and carbonyl structures. Condensed diarylmethane and carboxylic acid lignin structures were enriched and/or formed, particularly under aggressive oxygen conditions.

INTRODUCTION

Kraft pulping, oxygen delignification, and subsequent bleaching processes all interact and should be considered on a "system approach" basis to meet environmental and cost constraints. The trend in recent years toward low kappa pulping has resulted in lower bleaching costs due to decreased brownstock kappa number entering the bleach plant. Alternatively, a higher proportion of delignification can be shifted to the (multiple–stage) oxygen delignification stage by cooking the pulp to a higher kappa number. Oxygen delignification is more selective than the kraft cook process and potentially an increased final product yield can be realized [1-4]. The higher pulp yield can translate into a lower organic load to the recovery boiler, and for recovery–limited mills an increase in capacity can be achieved. A strong environmental incentive to use oxygen delignification is that it is chlorine–free and effluents are compatible with mill closure.

Peracetic acid is a TCF bleaching agent with excellent brightening properties [5]. The electrophilic bleaching agent is highly selective for delignification. Peracetic acid is being used at the mill level for TCF bleaching in Scandinavia [6, 7]. In Scandinavia, the bleaching agent is transported chilled in diluted form [5, 7]. Conversely, DOT shipping regulations limit large–scale shipping of peracetic acid in the United States and the material has to be prepared on–site.

Peracetic acid can be used in either equilibrium or distilled form. The equilibrium form contains appreciable residual hydrogen peroxide. Unless metals are sequestered, the residual peroxide can damage pulp viscosity. Distilled peracetic acid contains low residual peroxide content and pulp damage is much less likely. Peracetic acid [8, 9] and other peracids [10] can "activate" or increase the efficiency of a subsequent oxygen stage, although the fundamental reasons for this effect are not yet clear.

The broad goal of this study was to consider oxygen delignification and a low capital implementation of peracetic acid activation to improve oxygen delignification. Pulp parameters were studied after various PaO delignification conditions for both low and high kappa pulps. A specific focus was to use a range of novel and standard NMR methods to structurally analyze residual lignins and understand the fundamental chemistry of oxygen delignification/peracetic acid activation.

EXPERIMENTAL

Chemicals

All chemicals were commercially purchased and used as received except for 1,4–dioxane, which was purified by distillation over sodium borohydride.

Furnish
Pulps were prepared from a single softwood wood source which was chipped and screened with accepts between 3 and 8 mm. The chips were cooked under conventional kraft conditions in the laboratory to give two brownstock pulps of kappa number 24.0 (L/W = 4.5, EA% = 21, S% = 28.9, H = 2209) and 47.1 (L/W = 4.5, EA% = 19, S% = 28.9, H = 1200).

Peracetic Acid Treatment
Distilled peracetic acid (Pa) was prepared by simple vacuum distillation of equilibrium peracetic acid. The distilled peracetic acid was analyzed according to Greenspan and MacKellar [11] and found to have the following typical composition: Pa 29%, hydrogen peroxide 0.9%, and acetic acid 52%. Pulps were treated at a 4% charge of peracetic acid at 6% consistency in sealed polyethylene bags. The pH of the medium was adjusted to ~8 with alkali. The pulp was treated at 70°C for one hour. After treatment, pulps were thickened by dewatering using a Büchner funnel and were not washed before oxygen delignification.

Oxygen Delignification
A series of oxygen delignified (O) pulps were prepared from brownstock and peracetic acid pretreated pulps. In a modified digester, the following basic oxygen delignification conditions were used: 5.5% consistency, final pH >10.5, 75 psig oxygen, and 60–minute reaction. Specific details of the peracetic acid/oxygen delignification experiments and bleaching sequence abbreviations are given in Table 1. Bleached pulps were washed and characterized by kappa number (TAPPI 236 om–85), CED viscosity (TAPPI 230 om–94), and brightness (TAPPI 205 sp–95).

Table 1. Oxygen delignification conditions and bleaching sequence abbreviations.

Bleach sequence abbreviation	Bleaching conditions [a]
BS(47)	brownstock, kappa = 47
BS(47)O	oxygen delig.: 2.3% alkali charge, 90°C
BS(47)O*	oxygen delig.: 4.2% alkali charge, 105°C
BS(47)PaO	peracetic acid: 4% charge, oxygen delig.: 2.3% alkali charge, 90°C
BS(47)PaO*	peracetic acid: 4% charge, oxygen delig.: 4.2% alkali charge, 105°C
BS(47)OO	double oxygen delig.: 2.3% alkali charge, 90°C each stage
BS(47)OPaO	oxygen delig.: 2.3% alkali charge, 90°C, peracetic acid: 4% charge, oxygen delig.: 2.3% alkali charge, 90°C
BS(24)	brownstock, kappa = 24
BS(24)O	oxygen delig.: 1.3% alkali charge, 90°C
BS(24)O*	oxygen delig.: 2.2% alkali charge, 105°C
BS(24)PaO	peracetic acid: 4% charge, oxygen delig.: 1.3% alkali charge, 90°C
BS(24)PaO*	peracetic acid: 4% charge, oxygen delig.: 1.3% alkali charge, 105°C

[a] for additional conditions see experimental text.

Residual Lignin Isolation
Residual lignin was extracted from the pulp samples by an acidic 1,4–dioxane isolation procedure previously reported [12, 13]. Prior to lignin isolation, pulps were Soxhlet extracted for 24 hours with acetone, washed with water and air–dried. Lignin was extracted from the pulp with a 90% 1,4–dioxane/0.1 N HCl (v/v) solution (10% consistency) by refluxing for 2 hours under an argon atmosphere. The mixture was then filtered, concentrated, and purified by precipitation. Isolated lignin yields ranged from 37–57% relative to pulp kappa number. Purified lignin was freeze–dried and used for further analysis.

Functional Group Quantification
Lignin functional groups were determined by ^{1}H–, ^{13}C–, ^{19}F–, and ^{31}P–NMR using a Bruker 400 MHz NMR spectrometer. Proton–NMR spectroscopy was performed according to Li and Lundquist [14] using anhydrous DMSO–d_6 as the solvent and 3–(trimethylsilyl)propionate–2,2,3,3–d_4 as the internal standard. Carbon–13 NMR spectroscopy was employed according to the procedure of Robert [15] using integration regions consistent with the literature [15-17].

Lignin–hydroxyl groups were measured by using a modification of the phosphorus–NMR–based procedure previously reported [18-23]. Lignin, 35 mg, was completely dissolved in 280 μL pyridine containing chromium–acetylacetonate (2 mg/mL) and cyclohexanol (2 mg/mL), then 175 μL $CDCl_3$ was added. Fifteen minutes before NMR analysis, 75 μL 2–chloro–4,4,5,5–tetramethyl–1,3,2–dioxaphospholane (TMDP) was added to the lignin solution with stirring. Phosphorous–NMR analysis indicated that excess derivatization reagent was present in the solution (δ 176.0 ppm). NMR analysis was performed using the following conditions: 30° pulse angle, 25–second pulse delay, inverse–gated decoupling, and 200 scans per spectrum. Integration regions consistent with published data and model compound studies were used [18-22], and the baseline was locally corrected about the internal standard (cyclohexanol).

The *ortho*– and *para*–quinone contents of isolated lignins were quantified by ^{31}P–NMR spectroscopy after trimethylphosphite derivatization [24-27]. Lignin, 35 mg, was treated with 500 μL 50% trimethylphosphite/DMF (v/v) under argon. After two days, excess trimethylphosphite was removed by adding 250 μL DMSO and applying vacuum at 45°C until the sample was nearly dry. Treated lignins were dissolved in 400 μL 60% DMSO–d_6/pyridine (v/v) containing tri–*meta*–tolylphosphate (0.7 mg/mL, δ -16.3 ppm *vs.* 85% H_3PO_4, T_1 = 0.8 sec.) and chromium–acetylacetonate (0.9 mg/mL). Then 5 μL water was added to the sample and after 12 hours, the ^{31}P–NMR spectrum was acquired. Quantitative ^{31}P–NMR spectra were acquired using: 90° pulse, 5–second pulse delay, inverse–gated broad–band proton decoupling, and 1500 scans per spectrum. Lignin–quinone quantification was achieved using the following integration areas: tri–*meta*–tolylphosphate (internal standard) δ -14.9 to -17.4 ppm, and the quinone adduct δ -0.3 to -7.0 ppm.

Lignin–carbonyl groups were determined by using a modification of the ^{19}F–NMR procedure developed by Sevillano *et al.* [28, 29]. Lignin, 60 mg, was dissolved in 500 μL DMF, then 1 mL 50% DMF/water (v/v) containing 110 mg 4–trifluoromethylphenylhydrazine was added. After 12 hours, the derivatized lignin was precipitated by the addition of ~ 20 mL of water (pH = 2.0). The aqueous layer was discarded and the lignin was freeze–dried. The resulting lignin was Soxhlet extracted with CH_2Cl_2 for 2 hours then dried by vacuum over P_2O_5. Approximately 25 mg of derivatized lignin was dissolved in 450 μL DMSO–d_6 containing 3–trifluoromethoxybenzoic acid (0.5 mg/mL, δ -57.2 ppm *vs.* CCl_3F, T_1 = 1.6 sec) as an internal standard. NMR analysis was performed under the following conditions: 90° pulse angle, 10–second pulse delay, and 400 scans per spectrum. Lignin–carbonyl quantification was achieved by lineshape analysis using NUTS NMR Transform Utility Software (Acorn–NMR).

RESULTS AND DISCUSSION

Pulp Properties

Both kappa 24 and 47 brownstock pulps were oxygen delignified under various conditions. Oxygen delignification was targeted at two levels ~ 42% or "standard" delignification (O) and an "aggressive" degree of delignification (~ 68%, O*) employing additional alkali and higher temperature. Selected experiments used peracetic acid pretreatment before oxygen delignification. Peracetic acid treatment was performed at pH ~ 8 and pulps were not washed before subsequent oxygen delignification. The peracetic acid pretreatment method was selected so that it could easily be implemented at the mill level. Potentially, brownstock may be Pa treated without pH adjustment, using 1 hour treatment time, moderate temperature (70°C), and only dewatering (without washing) before the oxygen delignification stage. Figures 1–4 give pulp property data for the series of Pa/O pulps.

Note in Figure 1 that in comparison, the kappa 47 brownstock pulps gave higher brightness values than the kappa 24 pulps. Although a limited and low brightness range was studied, from Figure 1 we can see that the high and low kappa pulps follow parallel curves with the kappa 47 brownstock pulps brighter at any given kappa number. A similar effect was noted by Gajdos [4] and Steffes *et al.* [30] who also found that high kappa pulps gave greater brightness values after oxygen delignification.

Referring to Figure 1, peracetic acid pretreatment between two oxygen stages results in greater kappa reduction relative to the OO sequence. Other researchers have noted the activating influence of peracetic acid applied between two oxygen stages [31]. Peracetic acid pretreatment also allows for the decreased kappa number after subsequent oxygen delignification. For the kappa 47 pulp, peracetic acid pretreatment followed by aggressive oxygen delignification (BS(47)PaO*) gave higher pulp viscosity, similar kappa number, and slightly lower brightness than interstage pretreatment (BS(47)OPaO).

On the basis of viscosity *versus* brightness (Figure 2), the high kappa pulp showed higher viscosity at any given brightness value. Apparently the high intrinsic viscosity of the kappa 47 pulp is preserved during oxygen delignification. Steffes *et al.* noted that viscosity selectivity (Δ visc./ Δ kappa) is relatively constant for oxygen delignification over the pulp kappa number 18.9–57.1 [30]. Generally, 50% delignification is taken to be a rule of thumb as the maximum delignification that can be achieved without unacceptable loss of viscosity. For this study, the kappa 47 pulp can adequately withstand > 50% oxygen delignification because of its higher intrinsic viscosity.

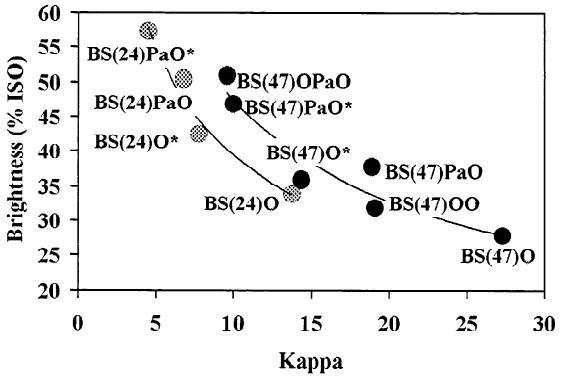

Figure 1. PaO pulp brightness/kappa properties.

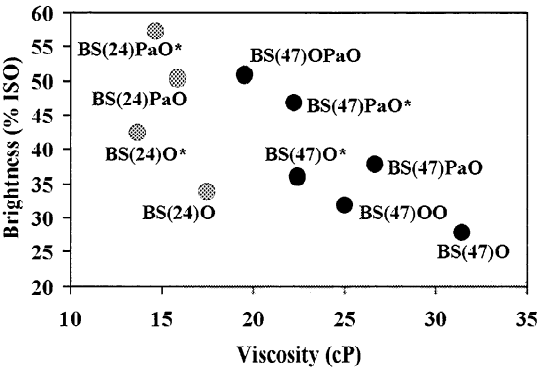

Figure 2. PaO pulp brightness/viscosity properties.

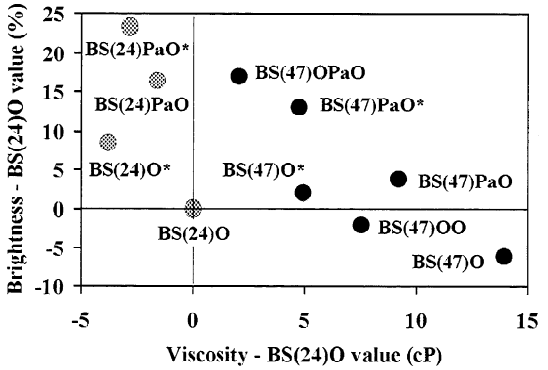

Figure 3. Pulp properties relative to the BS(24)O standard pulp.

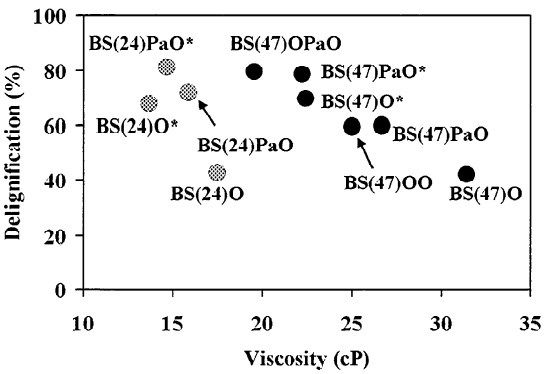

Figure 4. Bleachability of PaO pulps.

Residual Lignin Functional Group Contents

Quinone group contents. *Ortho*– and *para*-quinone lignin structures are potentially important groups to consider during bleaching because they are highly colored. Quinone structures are widely thought to be the major colored bodies present in a wide range of pulps and lignins [25, 32-38]. Recently our group demonstrated that chlorine dioxide dramatically increases the lignin–quinone content relative to the brownstock value [24-26]. DE*DED residual lignin quinone contents were found to correlate with pulp brightness and brightness ceiling values suggesting these structures may hinder brightness development [25]. Quinone structures have also been implicated in the alkali darkening reaction of mechanical [39] and chemical pulps [24].

Lebo *et al.* [40, 41] and Argyropoulos *et al.* [42] developed and used trimethylphosphite derivatization for the study of *ortho*–quinone structures in mechanical pulps. Both phosphorus microanalysis and qualitative solid–state ^{31}P–NMR spectroscopy were used to investigate derivatized mechanical pulps. Recently, trimethylphosphite derivation/^{31}P–NMR was extended for the simultaneous determination of both *ortho*– and *para*–quinone structures in isolated lignins [24-26, 43-45]. The method is currently in the process of development, but experimental evidence indicates quantitative results can be acquired, provided sample derivatization takes place under dry conditions [26, 43, 46, 47].

Figure 5 displays the quinone contents, measured by ^{31}P–NMR spectroscopy, for a series of residual lignins isolated from Pa/O pulps. In contrast to previous reports on chlorine dioxide bleaching [24-

26], the quinone contents were found to be uniformly low regardless of the exact oxygen delignification or peracetic acid pretreatment conditions used.

Oxygen/alkali can potentially cause the formation of quinone products from phenolic–lignin precursors by Dakin or Dakin–like reactions [48]. The result of this investigation supports model compound studies [48-50], which indicate that quinone intermediates are unstable and further oxidized to muconic acid and other structures. From a UV/Visible spectroscopy–based investigation, Pasco and Suckling speculated that simple quinone structures may not be the sole cause of visible–region absorbance in oxygen/alkali treated kraft lignins [36]. Therefore, the low quinone content measured in the Pa/O residual lignins appears to indicate that these structures may not be the major chromophores present in oxygen delignified pulps.

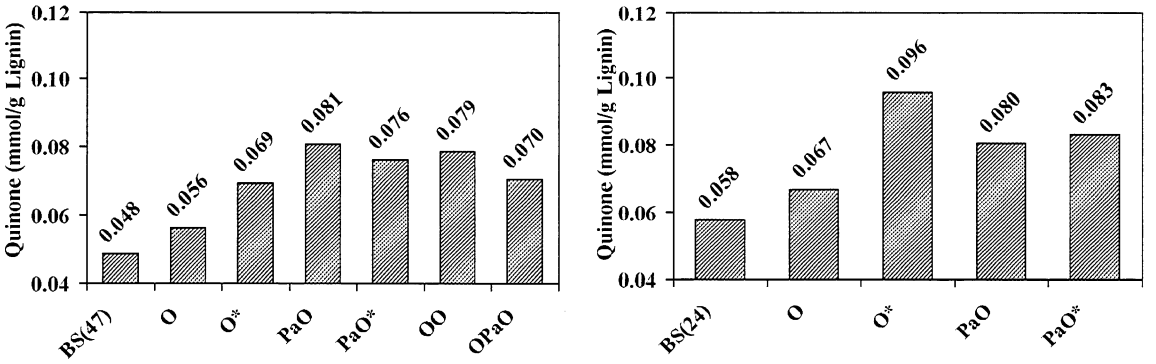

Figure 5. *Ortho–* and *para–*quinone contents of residual lignins from kappa 24 and 47 Pa/O pulps.

In a preliminary study, the quinone content values determined by trimethylphosphite/^{31}P–NMR were verified by applying the ^{19}F–NMR method developed by Sevillano *et al.* [28, 29]. For example, the quinone content for periodate and chlorine dioxide (KF = 0.2) residual lignins were found to be 0.503 and 0.322 mmol/g lignin respectively by ^{19}F–NMR (Figure 6), and 0.431 and 0.302 ± 0.004 (LSD = 0.02) mmol/g lignin by ^{31}P–NMR. Similarly, the quinone contents for kappa 47 Pa/O residual lignins determined by both ^{19}F– and ^{31}P–NMR are also close in value (Figures 5 and 6). Notable exceptions are the values determined for BS(47) and BS(47)O lignin samples; ^{19}F–NMR values are 3.3 and 1.7 times higher, respectively, than the ^{31}P–NMR values (Figures 5 and 6). The ^{19}F–NMR–derived results for BS(47) and BS(47)O residual lignins were replicated.

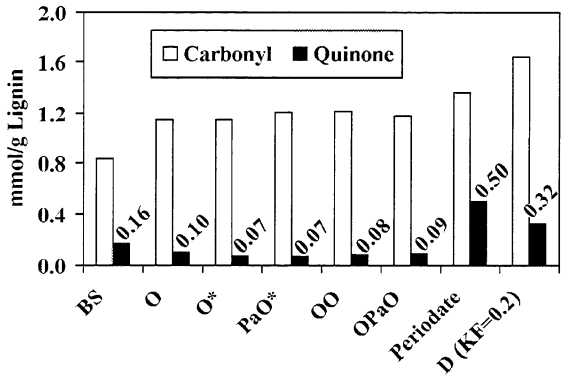

Figure 6. Carbonyl and quinone contents of BS(47) Pa/O residual lignins as determined by ^{19}F–NMR.

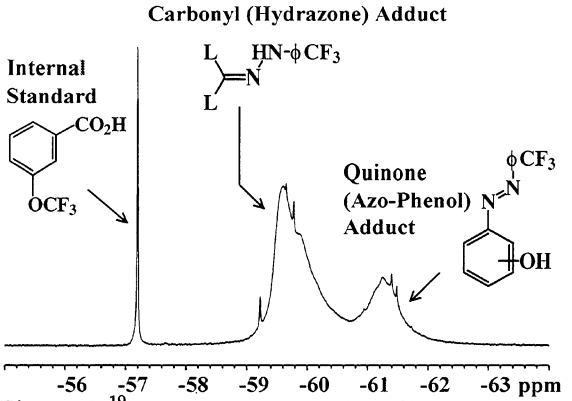

Figure 7. ^{19}F–NMR spectrum of 4–trifluoromethyl–phenylhydrazine treated periodate lignin.

For accurate results, the ^{19}F–NMR method relies on the formation of the azo(–phenol) derivative ($\delta \sim -61.2$ ppm) for quinones and the hydrazone derivative ($\delta \sim -60.5$ ppm) for other carbonyl structures (Figure 7, *cf.* [51, 52] re. azo–phenol/hydrazone tautomerism). Note, the ^{19}F–NMR method [28, 29] has been verified on a small number of model compounds. The ^{19}F–NMR methodology should be applied to

additional non–quinone carbonyl compounds to confirm that only derivatized quinone structures can exist in the azo tautomer. Additionally, the influence of sample preparation conditions on the potential oxidation of lignin–hydrazone to the azo form is not yet known. Otherwise, the close correspondence of ^{19}F– and ^{31}P–NMR values serves to verify both methods for the determination of quinones in lignins.

Carbonyl group contents. The ^{19}F–NMR method was useful for the determination of lignin–carbonyl functional groups. For kappa 47 Pa/O residual lignins, application of oxygen caused an increase in carbonyl content above the brownstock value but very little difference in carbonyl content was observed between the individual Pa/O lignins (Figure 6). The result for the BS(47)O residual lignin is similar to carbonyl content data determined by Lachenal *et al.* for an oxygen–stage residual lignin (BS kappa 30, 53% delig., C=0 content of 0.16/200g lignin ≈ 0.9 mmol/g lignin) [53].

H(1)– and P(31)–NMR derived data. Figures 8 and 9 show a comparison of ^{1}H–NMR and ^{31}P–NMR/TMDP derived residual lignin functional group data. Generally, the correlation between ^{1}H– and ^{31}P–NMR derived data was very good. A surprising result of this study is that the total phenolic content of the Pa/O residual lignins does not dramatically decrease with the application of aggressive oxygen, double–oxygen, or interstage peracetic acid conditions. From model compound studies, a dramatic decrease in total phenolic content would be expected because of the known reactivity of oxygen with phenolate structures [54], although these results are consistent with other residual lignin studies [55].

McDonough and Rapson [56] reported that peracetic acid under alkaline conditions degrades phenolic structures to a plethora of acid products. The reaction proceeds by electrophilic attack of peracetic acid on the phenolate, demethylation, and finally nucleophilic attack of peracetate on the *ortho*–benzoquinone intermediate. Additionally, alkaline peracetic acid may cause lignin side–chain oxidation, Baeyer–Villiger rearrangement to an aromatic ester, hydrolysis, and degradation to acid products [57]. During this study, the ability of peracetic acid to cause phenolic structures degradation was not readily apparent in the ^{1}H– and ^{31}P–NMR data (Figures 8 and 9). Only a marginal decrease in phenolic content as a result of peracetic acid pretreatment was observed (for example, BS(24)O* *versus* BS(24)PaO*, Figure 8).

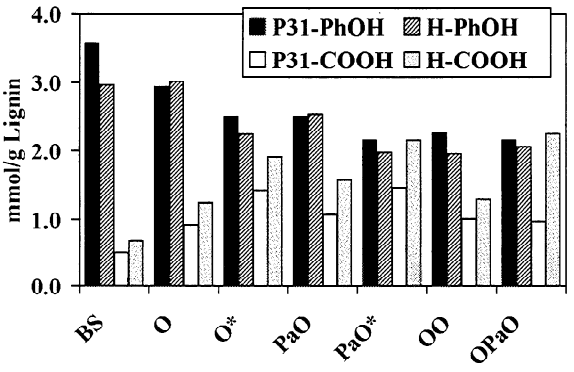

Figure 8. Comparison of ^{1}H– and ^{31}P–NMR determined OH functional group contents: BS(47) Pa/O residual lignins.

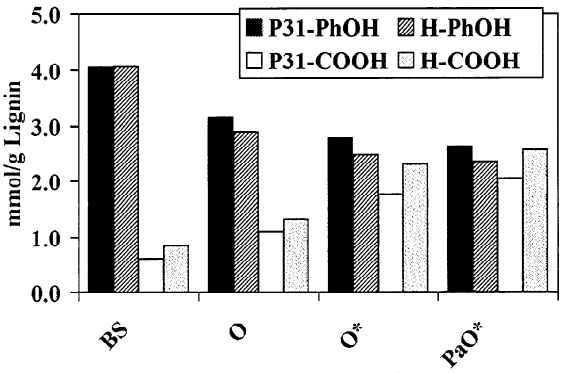

Figure 9. Comparison of ^{1}H– and ^{31}P–NMR determined OH functional group contents: BS(24) Pa/O residual lignins.

Overall, oxygen delignification, especially using aggressive conditions (O*, PaO*) or interstage peracetic acid treatment (OPaO), results in a dramatic increase in the lignin carboxylic acid content as measured by ^{1}H– and ^{31}P–NMR techniques (Figures 8 and 9). The increase in carboxylic acid content is consistent with model compound investigations, which have shown ring–opening and side–chain elimination reactions resulting in carboxylic acid formation [54]. Similarly, Gellerstedt *et al.* [55] and Argyropoulos *et al.* [58] and others have noted that oxygen delignification introduces carboxylic acid structures into lignin.

Referring to Figures 8 and 9 the residual lignin carboxylic acid contents determined by ^{1}H–NMR were consistently higher than those determined by ^{31}P–NMR. The deviation is particularly large for the BS(47)OPaO residual lignin (Figure 8). From preliminary model compound studies we found that the ^{31}P–NMR method may underestimate the presence of some hydroxyl functional groups, such as α–hydroxy

acid structures. Related side reactions have been reported by Argyropoulos *et al.* [59] and others [60]. Potentially, the ^{31}P–NMR carboxyl content value for the BS(47)OPaO residual lignin is lower than the ^{1}H–NMR value because of the presence of structures such as α–hydroxy acids that are not quantitatively derivatized. Further work needs to be done to determine the fundamental reason for the deviation of ^{1}H– and ^{31}P–NMR determined carboxylic acid content values for the BS(47)OPaO residual lignin.

C(13)–NMR derived data. Carbon(13)–NMR data is considered to be semiquantitative, because functional group data is expressed on a carbons per aromatic ring basis. Figure 10 and Table 2 give ^{13}C–NMR determined functional group data for both kappa 24 and 47 Pa/O residual lignins.

Diarylmethane–lignin structures can easily be detected by ^{13}C–NMR spectroscopy. The signal due to this "condensed" lignin substructure can be observed as a sharp signal at δ ~ 29 ppm [55]. Diarylmethane structures are known to be formed by the phenol–formaldehyde reaction [61]. Formation of diarylmethane structures have been reported from the alkali treatment of guaiacylglycerol–β–aryl ether model compounds [62]. Also, vanillyl alcohol has been reported to undergo condensation *via* a quinonemethide intermediate to give diarylmethane structures [63, 64]. Interestingly, diarylmethane structures have been shown to undergo air oxidation to give chromophoric extended quinonemethide structures stable to borohydride reduction [62-64]. Lai has indicated that diarylmethane structures are resistant to oxygen/alkali degradation relative to uncondensed structures [65].

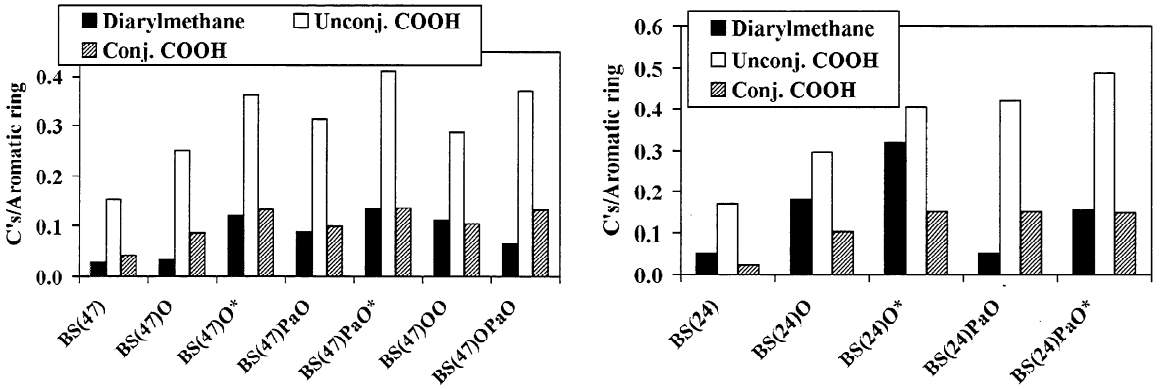

Figure 10. ^{13}C–NMR functional group data for residual lignins from PaO pulps.

Figure 10 shows the distribution of diarylmethane structures in the Pa/O residual lignins. From Figure 10 we can see that the content of diarylmethane structures is apparently greater in BS(24) pulps. Interestingly, the application of oxygen (BS(24)O), and particularly under aggressive conditions, (BS(24)O*) causes a dramatic increase and/or enrichment of these condensed structures. In the case of the BS(24) pulps, peracetic acid pretreatment appears to prevent the accumulation of the condensed diarylmethane structures. The influence of peracetic acid pretreatment is less clear on BS(47) pulps, although the diarylmethane content is greater in the BS(47)OO *versus* BS(47)OPaO residual lignin.

The data in Figure 10 also demonstrate the introduction of conjugated and unconjugated carboxylic acid structures into the residual lignin as a result of oxygen and peracetic acid treatment. The trend of the data is consistent with the results gained by ^{1}H– and ^{31}P–NMR spectroscopy (Figures 9 and 10). Again, aggressive oxygen conditions are more effective for lignin carboxylic acid group formation. Peracetic acid pretreatment appears to have a beneficial effect on the introduction of carboxylic acid groups, consistent with its reported chemistry [56, 57].

Additional lignin functional group data are assembled in Table 2. Differences in the Cγ (CH_2OH) carbon content were observed. A decrease in this functional group could potentially indicate the elimination of formaldehyde during oxygen delignification. Subsequently, the formaldehyde can participate in the formation of diarylmethane structures. Interestingly, the Cγ content appears to increase with oxygen delignification and particularly when the pulps are pretreated with peracetic acid. Generally, there was a noted increase in all aliphatic carbon functional groups as a result of oxygen delignification/peracetic acid treatment.

Table 2. ^{13}C–NMR data for Pa/O residual lignins (values expressed as carbons/aromatic ring).

Structure	BS(47)	O	O*	PaO	PaO*	OO	OPaO
Aliphatic C-O: Cβ in β-O-4; Cα in β-5 and β-β	0.32	0.35	0.43	0.44	0.50	0.40	0.47
Aliphatic C-O: Cα in β-O-4	0.33	0.35	0.46	0.46	0.52	0.40	0.49
Aliphatic COR	0.07	0.07	0.08	0.09	0.10	0.07	0.08
Aliphatic C-O: Cγ in β-O-4	0.17	0.16	0.18	0.21	0.20	0.18	0.20
Methoxyl OCH_3	0.77	0.76	0.75	0.78	0.76	0.75	0.76
Cβ in β-β and Cβ in β-5	0.06	0.06	0.06	0.06	0.06	0.05	0.06

Structure	BS(24)	O	O*	PaO	PaO*
Aliphatic C-O: Cβ in β-O-4; Cα in β-5 and β-β	0.22	0.24	0.30	0.36	0.38
Aliphatic C-O: Cα in β-O-4	0.24	0.30	0.36	0.41	0.45
Aliphatic COR	0.04	0.04	0.04	0.04	0.05
Aliphatic C-O: Cγ in β-O-4	0.10	0.10	0.10	0.13	0.12
Methoxyl OCH_3	0.70	0.67	0.64	0.67	0.68
Cβ in β-β and Cβ in β-5	0.04	0.04	0.02	0.40	0.02

CONCLUSIONS

Lignin functional group data revealed little quinone and carbonyl content differences between the various Pa/O residual lignins. The contents of these potentially chromophoric structures do not appear to be extensively altered by the oxygen delignification conditions. The data suggest that quinone and carbonyl lignin structures may not be major chromophoric structures and therefore may not have an impact on pulp brightness. The detected quinone contents were very low for all residual lignins studied. Carbonyl group contents did not vary appreciably for the kappa 47 Pa/O residual lignins. Further work remains to be done to understand the fundamental nature of brightness differences between the kappa 24 and 47 Pa/O pulps.

Standard ^{1}H–, ^{13}C–, and ^{31}P–NMR analyses of the residual lignins revealed that diarylmethane and carboxylic acid structures are enriched and/or formed as a result of Pa/O treatment. Surprisingly, the total phenolic contents of the residual lignins were lowered, but not dramatically by Pa/O treatment. Possibly, lignin phenolic structures are more resistant toward oxygen delignification and peracetic acid than has been suggested by previous model compound studies.

Potentially, oxygen delignification can be interpreted as a wholesale removal of lignin fragments with little apparent evidence of the delignification mechanism residing in structural features of the (residual) lignin left in the pulp. Similarly, Gellerstedt *et al.* interpreted the unexpectedly low level of observed lignin structural changes after oxygen delignification in the following manner: "...bleaching seems to follow a pattern which resembles the peeling of an onion layer by layer and, once a layer has been chemically modified and removed, the lignin is again reactive and available for new chemical attack. [55]"

Both low (24) and high (47) kappa softwood kraft pulps were oxygen delignified under standard (~ 42% delig.) and aggressive (~ 68% delig.) conditions. A series of pulps were treated with distilled peracetic acid (pH = 8). Peracetic acid applied before and between oxygen delignification stages was beneficial and allowed for a greater kappa number reduction.

Apparently, under the conditions of application in this study, peracetic acid caused no loss of pulp viscosity. Generally, 50% delignification is taken to be a rule of thumb as the maximum delignification that can be achieved without unacceptable loss of viscosity (pulp strength). Clearly, for this study the kappa 47 pulp could adequately withstand > 50% oxygen delignification and still give a pulp with properties similar to the standard case (BS(24)O).

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